PB-238 267

LABORATORY AND FIELD EVALUATIONS OF EPA METHODS 2, 6, AND 7

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Southwest Research Institute

Prepared for:

National Environmental Research Center

October 1973

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TECHNICAL REPORT DATA
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1. REPORT NO.	2.	PB 238 267
EPA-650/4-74-039		

4. TITLE AND SUBTITLE	5. REPORT DATE
"Laboratory and Field Evaluations of EPA Methods 2, 6, and 7."	October 1973
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Henry F. Hamil	SWRI Project 01-3462-001
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Southwest Research Institute, 8500 Culebra Rd., San Antonio, Texas 78284	1HA327
	11. CONTRACT/GRANT NO.
	68-02-0626
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Environmental Protection Agency, NERC, QAEML Methods Standardization & Performance Evaluation Branch Research Triangle Park, N. C. 27711	14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

A study was made to evaluate Methods 2, 6, and 7, proposed by EPA for determination of stack gas velocity and volumetric flow rate, sulfur dioxide emissions, and nitrogen oxide emissions. These evaluations were conducted prior to collaborative testing of the subject methods. Method 2: Stack Gas Velocity and Volumetric Flow Rate: Statistical analysis of stack gas velocity data indicates that Method 2 provides an accurate estimate of the true stack gas velocity at high gas velocities. Accuracy of Method 2 velocity estimates at low gas velocities is shown to be unreliable. Correlation analysis demonstrates that the volumetric flow rate estimates have the same characteristics as the velocity estimates. Correlation analysis also demonstrates that the variation in the stack gas velocity and volumetric flow rate estimates is principally due to variation in determination of Δp, the velocity head in the stack. By way of comparison, a separate analysis was performed on individual velocity traverse data. Method 6 - Sulfur Dioxide: Investigation of possible causes of variation in collection efficiency of SO_2 in Method 6 was made. Concentration of SO_2 in the stack gas is shown to be the only factor to have any significant effect on collection efficiency. The purge period specified in Method 6 was shown to be necessary to avoid apparent low SO_2 values due to retention in the isopropanol bubbler. The minimum limit is estimated to be 3 ppm. Method 7-Nitrogen Oxides: Investigation of possible interference with NO_x determination bychloride ion indicated the degree of interference to be linearly related to chloride ion concentration.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Accuracy, precision and detection limits are reported.		

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Springfield, VA. 22151

PRICES SUBJECT TO CHANGE

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Unlimited	Unclassified	64
	20. SECURITY CLASS (This page)	22. PRICE
	Unclassified	$4.25/2.25

EPA Form 2220-1 (9-73)

EPA-650/4-74-039

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Contract No. 68-02-0626
Task Order 1, Change Order 1
ROAP No. 26AAG
Program Element No. 1HA327

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Prepared for

OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

October 1973

This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

A study was made to evaluate Methods 2, 6, and 7, proposed by the Environmental Protection Agency for determination of stack gas velocity and volumetric flow rate, sulfur dioxide emissions, and nitrogen oxide emissions, respectively. These evaluations were conducted prior to collaborative testing of the subject methods. Findings and conclusions concerning these methods are given below.

Method 2 - Stack Gas Velocity and Volumetric Flow Rate

Statistical analysis of stack gas velocity data indicates that Method 2 provides an accurate estimate of the true stack gas velocity at high gas velocities. Accuracy of Method 2 velocity estimates at low gas velocities is shown to be unreliable. Correlation analysis demonstrates that the volumetric flow rate estimates have the same characteristics as the velocity estimates. Correlation analysis also demonstrates that the variation in the stack gas velocity and volumetric flow rate estimates is principally due to variation in determination of Δp, the velocity head in the stack. By way of comparison, a separate analysis was performed on individual velocity traverse data.

Method 6 - Sulfur Dioxide

Investigation of possible causes of variation in collection efficiency of SO_2 in Method 6 was made. Concentration of SO_2 in the stack gas is

shown to be the only factor to have any significant effect on collection efficiency. The purge period specified in Method 6 was shown to be necessary to avoid apparent low SO_2 values due to retention in the isopropanol bubbler. The minimum detectable limit is estimated to be 3ppm.

Method 7 - Nitrogen Oxides

Investigation of possible interference with NO_x determination by chloride ion indicated the degree of interference to be linearly related to chloride ion concentration.

The minimum detectable limit for Method 7 is estimated to be 2 ppm NO_x as NO_2. The upper limit without dilution is approximately 100 ppm NO_x as NO_2. The maximum sensitivity of Method 7 can approach 0.2 ppm but probably lies between 0.2 ppm and 2.0 ppm NO_x as NO_2.

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I. INTRODUCTION

This report describes the work performed and the results obtained on Task Order No. 1, and Task Order No. 1, Change Order No. 1, which included evaluation of the methods for the determination of stack gas velocity and volumetric flow rate, the determination of nitrogen oxide emissions, and the determination of sulfur oxide emissions in fossil-fuel fired steam generators (Federal Register, December 23, 1971).

Complete plans were developed for the accomplishment of the objectives before the experimental work began. These plans were submitted to the Project Officer by letter dated October 3, 1972, and received subsequent approval.

The task order required experimental investigation of the following: Possible sources of error in determination of stack gas velocity and volumetric flow rate due to calibration of the type S pitot tube, and determination of precision and accuracy of the method in a suitable facility in which a theoretical value for velocity could be obtained.

The laboratory investigation of the sulfur dioxide method included an investigation of SO_2 collection efficiency as a function of changing concentration, as well as investigation of low recovery of SO_2 due to retention in the isopropanol bubbler.

The laboratory investigation of the nitrogen oxide method included an evaluation of the detection limits of the method and an investigation of possible chloride ion interference in the analysis.

A glossary of appropriate equations and terms used in this report is given in Appendix I.

II. RESULTS AND CONCLUSIONS

METHOD 2 - STACK GAS VELOCITY AND VOLUMETRIC FLOW RATE

1. Evaluation of Method 2

The stack gas velocity and volumetric flow rate as determined by Method 2 are used in conjunction with the methods for determination of specific pollutants to determine the emission rate of those pollutants. Therefore, evaluation of Method 2 with regard to precision and accuracy was considered necessary. The experimental program was structured to allow estimation of the precision and accuracy of Method 2. Statistical analysis of the data obtained in the experimental program was performed in order to determine which experimental variables contributed most to the variation in the stack gas velocity.

Permission was obtained from Houston Lighting and Power Company to perform a series of measurements at their T. H. Wharton Power Plant. This plant is a natural gas fired steam generating plant, normally maintained on hot standby, and is used to balance peak loads. As a result, arrangements could be made to make velocity traverse measurements at peak load and at a lower level, to give two different stack velocities during the evaluation.

The fuel gas feed rate is accurately measured at the T. H. Wharton Plant, and this value, in conjunction with stack gas composition as determined by Orsat analysis, allows the calculation of theoretical stack

gas velocities for comparison with the experimentally determined values. A sample calculation demonstrating the method used to determine the theoretical stack gas velocity and volumetric flow rate is shown in Appendix II.

Table 1 tabulates the pertinent operating characteristics of the power plant unit which was used for field investigations, while Tables 2 and 3 show the data obtained by pitot tube traverses at this facility, at the two feed rates studied.

TABLE 1. OPERATING CHARACTERISTICS
T. H. WHARTON POWER PLANT, UNIT NO. 1
HOUSTON LIGHTING & POWER COMPANY

Output:	75 megawatts
Fuel Consumption:	13,600 cu ft per minute, natural gas
Air Rate:	146,000 cu ft per minute
Steam Rate:	650,000 lb per hour, 1340 psi, 955°F
Stack Velocity:	52 ft per second
Sample Ports:	Two 3-in. ports at 90-degree spacing are located next to a walkway handrail at the 100-ft level (above grade). This location is 56 feet (8.3 diameters) above the preheaters for the boiler, Two 45-degree elbows in the vertical stack run affect the flow pattern somewhat, but the ports are still 24 feet (3.6 diameters) above the higher ell so that a reasonably uniform flow pattern should exist at the existing sample port elevation.

TABLE 2. VELOCITY TRAVERSE DATA,
HOUSTON LIGHTING & POWER CO., T. H. WHARTON POWER PLANT,
UNIT NO. 1, LOW FUEL FEED RATE[1]

Date	Run No.	Time	Δp_{avg} (in H_2O)	$(\sqrt{\Delta p})_{avg}$ (in $H_2O)^{1/2}$	T_s °F	T_s °F	P_s in Hg	% H_2O	% CO_2	% O_2	M_d	M_s	$V_{s_{avg}}$ fps	Q_s scf/hr x 10^{-6}
5/22/73	1	1125-1155	0.275	0.524	266	726	29.83	14.0	8.2	6.4	29.5	27.9	32.2	4.970
"	2	1210-1235	0.285	0.521	252	712	29.82	14.6	8.5	5.0	29.5	27.8	31.9	4.937
5/23/73	5	1025-1047	0.245	0.498	255	715	29.78	13.5	7.8	6.5	29.5	28.0	33.6	4.774
"	6	1055-1130	0.265	0.513	251	711	29.77	14.0	8.2	6.3	29.5	27.9	31.8	4.914
"	7	1135-1200	0.265	0.517	264	724	29.77	14.0	8.2	6.4	29.5	27.9	32.4	4.911

[1]Definition of symbols is given in Appendix I.

TABLE 3. VELOCITY TRAVERSE DATA,
HOUSTON LIGHTING & POWER CO., T. H. WHARTON POWER PLANT,
UNIT NO. 1, LOW FUEL FEED RATE[1]

Date	Traverse No.	Time	Δp_{avg} (in H_2O)	$(\sqrt{\Delta p})_{avg}$ (in $H_2O)^{\frac{1}{2}}$	T_s ^oF	T_s ^oR	P_s in Hg	$\%H_2O$	$\%CO_2$	$\%O_2$	M_d	M_s	$V_{s\,avg}$ fps	Q_s scf/hr x 10^{-6}
5/22/73	3	1400-1425	0.88	0.912	307	767	29.80	14.9	8.8	5.5	29.6	27.9	57.6	8.318
"	4	1428-1455	0.82	0.878	317	777	29.80	14.3	8.4	5.8	29.6	27.9	55.8	8.021
5/23/73	8	1340-1400	0.89	0.937	300	760	29.73	14.7	8.6	4.9	29.5	27.8	59.2	8.683
"	9	1405-1425	0.89	0.937	310	770	29.73	17.1	8.9	5.4	29.6	27.6	59.8	8.370

[1]Definition of symbols is given in Appendix I.

The sample ports, designated east (E) and west (W) are located 90° apart on both stacks A and B (see Figure 1). The total gas flow from the unit is split at the preheater outlet and vented through the two stacks of 80-in. I.D.* Since there is a disturbance approximately 3.6 diameters upstream of the sample ports, 24 traverse points were chosen on each diameter.

The Type S pitot tube was calibrated in a wind tunnel at Southwest Research Institute. Calibration was performed over a velocity range of 17 to 70 fps. At velocities in that range, the pitot tube coefficient C_p had an average value of 0.77. Variation of the coefficient over the working range was within the ± 5% specified in the method. The coefficient was determined with each leg of the pitot tube facing the gas flow and was found to be the same in each case.

Data were taken on two days, at two different generating levels each day. The higher generating level of 71.0 megawatts was near the rated peak generating level of 72 megawatts, while the lower level was 40.0 or 41.5 megawatts. On the second day, two traverses were made during unit line-out while the generating levels were 39.0 and 42.0 megawatts. The remaining lower level generating loads were 40.0 megawatts after line-out.

Fuel feed rates were 680 MCFH at the 71 megawatt generating level and 385-390 MCFH at the 40-41.5 megawatt generating level.

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*EPA policy is to express all measurements in Agency documents in metric units. When implementing this practice will result in undue cost or difficulty in clarity, NERC/RTP is providing conversion factors for the particular non-metric units used in the document. For this report these factors are located in Appendix I.

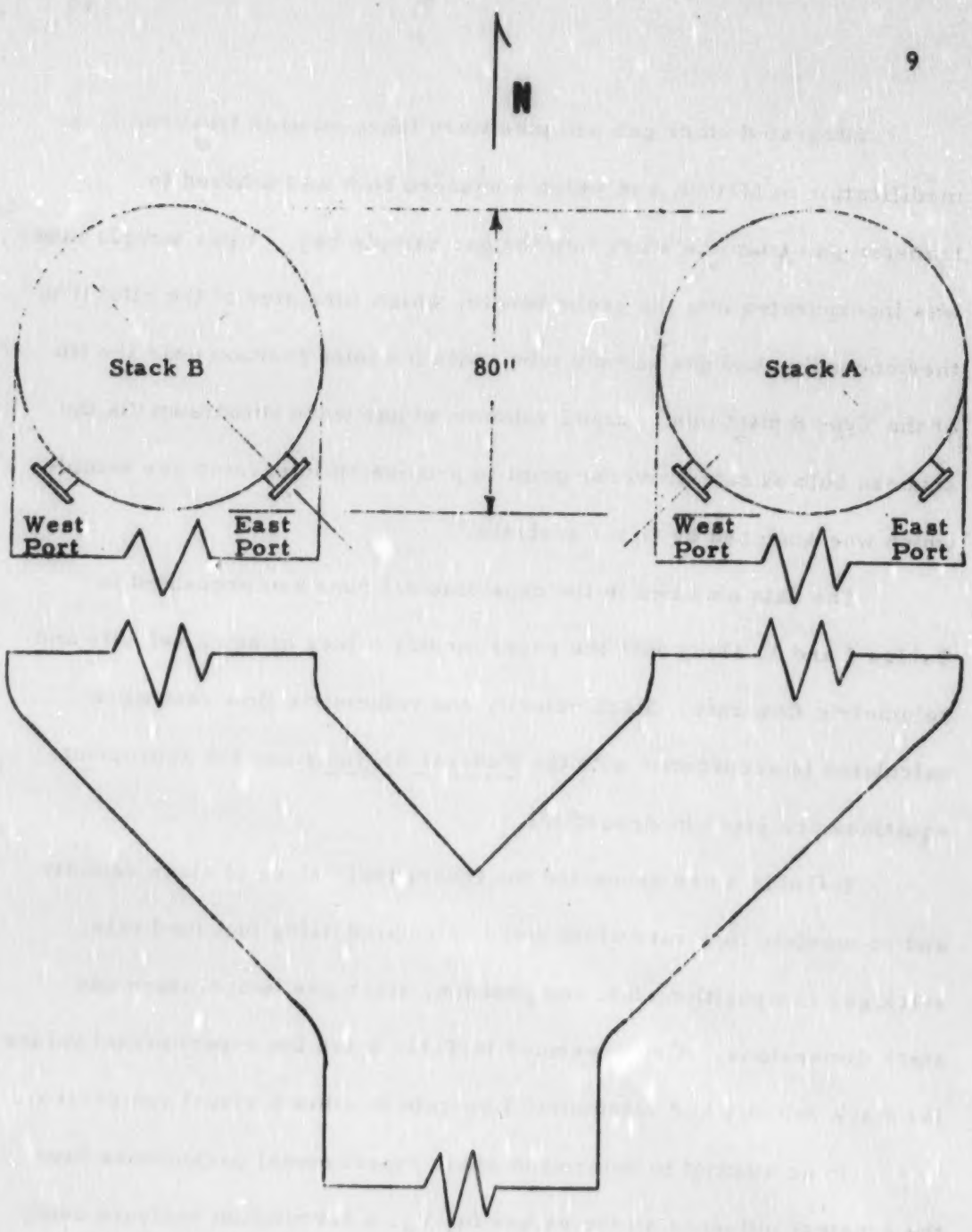

FIGURE 1. T. H. WHARTON PLANT, UNIT NO. 1,
SAMPLE PORT CONFIGURATION

Integrated stack gas samples were taken on each traverse by a modification of Method 3 in which a squeeze bulb was utilized to transfer gas from the stack into the gas sample bag. A gas sample tube was incorporated into the probe bundle, which consisted of the pitot tube thermocouple, and gas sample tube, with the inlet position near the tip of the Type S pitot tube. Equal volumes of gas were withdrawn via the squeeze bulb at each traverse point to provide an integrated gas sample which was analyzed by Orsat analysis.

The data obtained in the experimental runs are presented in Tables 2 and 3, along with the experimental values of stack velocity and volumetric flow rate. Stack velocity and volumetric flow rate were calculated in accordance with the Federal Register, and the appropriate equations are given in Appendix I.

In Table 4 are presented the theoretical values of stack velocity and volumetric flow rate which were calculated using fuel feed rate, stack gas composition, fuel composition, stack gas temperature and stack dimensions. Also presented in Table 4 are the experimental values for stack velocity and volumetric flow rate to allow a visual comparison.

In an attempt to determine which experimental parameters have the greatest influence on the values for V_s, a correlation analysis using the data in Tables 2 and 3 was performed using V_s as the dependent variable and Δp_{avg}, $(\sqrt{\Delta p})_{avg}$, T_s, P_s, and M_s as independent variables.

TABLE 4. EXPERIMENTAL AND THEORETICAL GAS VELOCITY AND VOLUMETRIC FLOW RATE - HOUSTON LIGHTING AND POWER COMPANY, T. H. WHARTON PLANT, UNIT NO. 1

Run No.[1]	Stack Designation[2]	Fuel Gas[3] Feed Rate MCFH	Load, megawatts	V Stack Gas Velocity, fps		Q Volumetric Flow Rate, scf/hr x 10^{-6}	
				Experimental	Theoretical[4]	Experimental	Theoretical[5]
1	A	390	41.5	32.2	32.9	4.970	5.197
2	B	390	41.5	31.6	31.9	4.937	5.134
3	B	680	71.0	57.6	56.5	8.318	8.443
4	A	680	71.0	55.8	59.8	8.021	8.975
5	A	385	40.5	30.3	33.6	4.774	5.393
6	B	385	40.0	31.2	31.8	4.914	5.130
7	A	385	40.0	31.8	32.4	4.911	5.130
8	A	680	71.0	59.2	57.3	8.683	8.639
9	B	680	71.0	59.8	56.1	8.370	8.348

[1]Run data are calculated from appropriate diameter traverse data, i.e., Run 1 from traverses 2AW + 1AE.
[2]Stack designation per Figure 1.
[3]Fuel gas volume is in cubic feet at 60°F and 1 atmosphere pressure.
[4]Calculated by the procedure shown in Appendix 1, wet gas basis.
[5]Calculated by the procedure shown in Appendix 1, dry gas basis.

The correlation coefficients obtained are presented in Table 5.

TABLE 5. CORRELATION COEFFICIENTS V_s AS A DEPENDENT VARIABLE OF VARIOUS EXPERIMENTAL PARAMETERS

Independent Variable, X	Correlation Coefficient, $V_s = f(x)$
ΔP_{avg}	0.9944
$(\sqrt{\Delta P})_{avg}$	0.9996
T_s, °R	0.9286
P_s, in. Hg	-0.4778
M_s	-0.3780

As can be seen from the values in Table 5, the strongest correlation is obtained with V_s as a function of $(\sqrt{\Delta P})_{avg}$ and of ΔP_{avg}. This correlation analysis shows a very strong linear relationship between V_s and these two related experimental parameters. The direct relationship of V_s to the other experimental parameters is less strong, based upon the correlation coefficients. From the correlation analysis, one would conclude that the variance in V_s would be most affected by the variance in $(\sqrt{\Delta P})_{avg}$, which relates directly back to the variance in ΔP_{avg}.

To further check this hypothesis, a simple statistical analysis of the experimental stack velocity and volumetric flow rate along with Δp_{avg}, $(\sqrt{\Delta p})_{avg}$, $T_{s_{avg}}$, M_s, and P_s was made in which the mean, variance, standard deviation, and percent distribution about the mean at 2s were calculated. The analysis was performed on the run data presented in Tables 2 and 3.

Percentage distribution about the mean at 2s (i.e., the 95% confidence level) is defined as $\frac{2s \cdot 100}{\bar{x}}$. It measures the amount of variation in the experimental data for variable x, expressed as a percentage of the mean value. Each of the independent experimental parameters being studied is directly or inversely proportional to V_s in the V_s equation. Thus, a valid technique for determining the parameters to which V_s is most sensitive, and to which its variability and its uncertainty are most closely related, is to compare the percentage distribution about the mean for V_s to the percentage distributions about the mean for the various independent experimental variables. For comparison, a similar analysis of the theoretical stack velocity was made along with the mole percent CO_2 in the stack gas and the stack gas temperature. These two parameters were chosen for the latter analysis inasmuch as they are the two experimentally determined numbers which have the most influence on the calculation of the theoretical velocity (see Appendix II). The portion of the analysis pertaining to Q_s is included to show the relationship between V_s and Q_s and between Q_s and the experimentally determined parameters.

For the statistical treatment, the data were divided into high and low levels corresponding to the power generating levels of 71.0 and 40.0-41.5 megawatts.

The results of the analysis are presented in Table 6, showing the mean, variance, standard deviation, and percentage distribution about the mean at the 95 percent confidence level.

TABLE 6. STATISTICAL ANALYSIS - EXPERIMENTAL STACK VELOCITIES AND RELATED PARAMETERS

Fuel Feed Rate	Variable x	Mean $\bar{x}$	Variance s^2	Standard Deviation s	Percent Distribution About the Mean $\frac{2s \times 100}{\bar{x}}$ 95% Confidence Limits
Low	V_s	31.4	0.57	0.756	4.8
	Q_s	4.901×10^6	$.0056 \times 10^{12}$	$.075 \times 10^6$	3.7
	$\Delta_{P_{avg}}$	0.26	0.0003	0.0175	13.5
	$(\sqrt{\Delta_p})_{avg}$	0.51	0.0001	0.01	3.9
	$T_{s_{avg}}$	717	52.0	7.21	2.0
	P_s	29.50	0.0	0.0	0.0
	M_s	27.9	0.005	0.07	0.5
High	V_s	58.1	4.06	2.015	6.9
	Q_s	8.348×10^6	0.0735×10^{12}	0.271×10^6	6.5
	$\Delta_{P_{avg}}$	0.87	0.001	0.032	7.4
	$(\sqrt{\Delta_p})_{avg}$	0.92	0.0004	0.02	4.3
	$T_{s_{avg}}$	768	44.0	6.6	1.8
	P_s	29.56	0.0023	0.048	0.3
	M_s	27.8	0.02	0.14	1.0

It can be seen that for Δp_{avg}, the values of s^2 and s are not the same at the high and low levels, indicating an inequality of variance at the levels studied. The percent distribution about the mean for Δp_{avg} is $\pm$ 13.5 at the low level and $\pm$ 7.4 at the high level. The percent distribution about the mean is related to the repeatability of the method of measuring Δp_{avg}. In this particular experiment, however, the true value of Δp in the stack is not known, and due to normal variations in process parameters the true value of Δp would be expected to vary with time. The natural variations in true Δp with time would contribute to the variance about the mean for the set of runs and as a result would be incorporated in the percent distribution about the mean, along with that variance about the mean attributable to the repeatability of the method.

Since no procedure is available for readily separating the effects of variation of true Δp with time from the effect of repeatability of the method in the statistical analysis, the percent distribution about the mean is considered a measure of the total uncertainty of the experimental values, and consists of the uncertainty due to variations in true Δp plus uncertainty due to repeatability of the method. However, it is believed that the flow conditions in the stacks at the test site are generally characteristic of conditions encountered in stack velocity measurements, and as a result, the data developed in this study are representative of the results which can be expected from use of Method 2.

The percent distribution about the mean for Δp_{avg} indicates that the total uncertainty in Δp_{avg} is considerably greater at low values of Δp_{avg} than at high values of Δp_{avg}. This is not unexpected in view of the behavior of the Type S pitot tube and inclined manometer when measuring velocity heads in disturbed flows. It has been our experience that when this measuring system is used in stacks where flow patterns are disturbed and/or cyclonic, oscillations are set up in the liquid column of the inclined manometer. The observed oscillations were 0.2-0.3 inches of water and were unsymmetric within the observed range. Readings of Δp at each traverse point are made by a visual estimate of the average value within the range of oscillation. The range of oscillation at a particular site does not appear to be a function of overall velocity. For example, in the study under discussion, the range of the manometer oscillation was essentially the same at stack gas velocities of about 31 and 58 fps.

As a result, the relative error in reading Δp is greater at low values where the range of oscillation of the manometer is approximately equal to the value of Δp than at high values of Δp where the range of oscillation is approximately one-half the value of Δp.

A brief study was made during pitot tube calibrations to determine if a Magnehelic(TM) differential pressure gauge, which

incorporates small orifices in the pitot line connections to provide damping of sudden transient pressures, was a suitable substitute for the inclined manometer. The flow in the wind tunnel was intentionally disturbed to simulate stack gas flow conditions. Even though the Magnehelic gauge is damped, resulting Δp measurements were no better than those obtained with an inclined manometer inasmuch as the Magnehelic gauge showed the characteristic oscillations described above.

Even though the total uncertainty in Δp_{avg} appears rather large at the lower values observed, the effect on the total uncertainty of the experimental stack velocity is minimized to a fair extent by the fact that $(\sqrt{\Delta p})_{avg}$ is used in the calculation of the velocity. The calculation of $(\sqrt{\Delta p})_{avg}$ from the individual Δp values measured at each traverse point is a transformation that both stabilizes the data and minimizes its random measurement variation. As can be seen in Table 6, equality of variance is not obtained for $(\sqrt{\Delta p})_{avg}$ over the range studied. Instead, s^2 and s appear to be a function of the level of $(\sqrt{\Delta p})_{avg}$. This is further shown by examination of the percent distribution about the mean for $(\sqrt{\Delta p})_{avg}$ at the high and low levels, where it can be seen that the total uncertainty is $\pm$ 3.9% at the low level and $\pm$ 4.3% at the high level. When the experimental stack velocity data in Table 6 are examined, it can be seen that s^2 and s also are a function of the level of V_s. The percent distribution about the mean velocity at the high and low levels is $\pm$ 6.9 and $\pm$ 4.8, respectively.

These values are in fair agreement with the similar values for $(\sqrt{\Delta p})_{avg}$ at the high and low levels, as would be expected from the highly linear relationship of these two variables indicated in the correlation analysis. The percent distribution about the mean for Q_s at the high and low levels is $\pm$ 6.5 and $\pm$ 3.7, respectively. These values correspond favorably with those same values for V_s and $(\sqrt{\Delta p})_{avg}$. A correlation analysis using $Q_s = f(V_s)$ gives a correlation coefficient of 0.9984, indicating a strong linear relationship between Q_s and V_s, which establishes the dependence of Q_s on those same parameters upon which V_s is dependent.

The other parameters used to calculate V_s are $T_{s(avg)}$, M_s, and P_s. The correlation analysis showed poorer linear correlation between these variables and V_s. This is supported by the statistical analysis of these parameters. As can be seen in Table 6, the percent distribution around the mean for these variables is small, indicating that the total uncertainty is small, and when variations in process parameters are considered to occur, this implies good repeatability for the determination of $T_{s(avg)}$, P_s, and M_s. Thus it would appear that the experimental parameter which most affects the value of V_s is $(\sqrt{\Delta p})_{avg}$.

The theoretical stack velocities were calculated as shown in Appendix II. From the calculation method used, it can be seen that the calculated theoretical velocities are dependent upon carbon in the fuel, carbon in the stack gas, fuel feed rate, stack gas temperature, and stack dimensions.

Fuel carbon analyses and fuel feed rates were provided by Houston Lighting and Power Company, and no estimate of accuracy or repeatability for these values is available. Fuel feed rates were measured with a calibrated orifice meter and were reported as cubic feet at 60°F and 1 atmosphere pressure. Carbon in the feed was calculated from a gas chromatographic analysis of the fuel gas and was reported as lb-atoms carbon per lb-mole fuel gas.

Carbon in the stack gas was obtained from the Orsat analysis of the integrated gas sample taken on each run. Stack temperature was also determined experimentally on each run. These two variables were subjected to statistical analysis along with the theoretical velocities.

In Table 7, it can be seen that the percent distribution about the mean for the theoretical velocity at the high and low levels is $\pm$ 5.8 and $\pm$ 4.6, respectively. The percent distribution about the mean for the theoretical volumetric flow rate at the high and low levels is $\pm$ 6.4 and $\pm$ 4.4, respectively. The percent distribution about the mean for CO_2 concentration at the high and low levels is $\pm$ 5.0 and $\pm$ 6.1, respectively. The distribution about the mean for T_s at the high and low levels is $\pm$ 1.8 and $\pm$ 2.0 percent, respectively. These values would appear to indicate that the experimental variable with greatest effect on the calculated values of theoretical velocities is the CO_2 content of the stack gas as determined by Orsat Analysis and that the accuracy of this experimental value is reflected in the accuracy of the theoretical velocities.

TABLE 7. STATISTICAL ANALYSIS, THEORETICAL STACK VELOCITIES AND RELATED PARAMETERS

Fuel Feed Rate	Variable x	Mean $\bar{x}$	Variance s^2	Standard Deviation s	Percent Distribution About the Mean $\frac{2s \times 100}{\bar{x}}$ 95% Confidence Level
Low	V	32.5	0.56	0.75	4.6
	Q	5.197×10^6	0.013×10^{12}	0.113×10^6	4.4
	$\%CO_2$	8.2	0.062	0.25	6.1
	T_s	717	52.0	7.21	2.0
High	V	57.4	2.75	1.66	5.8
	$\%CO_2$	8.7	0.05	0.22	5.0
	Q	8.601×10^6	0.077×10^{12}	0.277×10^6	6.4
	T_s	768	44	6.6	1.8

Statistical analysis performed on the volumetric flow rate data indicates they are primarily dependent on the stack gas velocity. The accuracy, repeatability and distribution about the mean for volumetric flow rates appear to be a direct function of the same parameters as for the velocity data.

In order to assess the accuracy of Method 2 determination of stack gas velocity, a comparison was made between the experimental and theoretical stack gas mean values at both the high and low levels. The details of the test are shown in Appendix 4.

At the low level, there was a significant difference between the experimental and theoretical mean values. At the high level, no significant difference between the experimental and theoretical mean values was indicated.

Based upon the assumption that the theoretical mean values represent the true stack gas velocities, velocity determinations by Method 2 as written provide a reasonable estimate of stack gas velocity at high velocity levels. However, at low velocity levels, the method does not provide a good estimate of stack gas velocity.

Since the statistical treatment previously described indicated that the accuracy and repeatability of Q_s appear to be a direct function of the same parameters as V_s, the above assessment of accuracy remains valid for Q_s at high and low levels.

2. Analysis of Single Traverse Data

As shown in the previous section, the limits of accuracy with which Δp can be measured at the individual traverse points will be the predominant factor in determining the accuracy of the values obtained for V_s, over the range studied.

It is believed that since the experimental stack velocity may be influenced by both time dependent variations due to changes in process parameters and by unsymmetrical flow geometry in the stack, a more accurate estimate of the repeatability of the procedure for determinating velocity could be obtained by statistical analysis of the data determined from traverses of a single diameter. The use of two diameter traverses may give a more accurate estimate of the time average velocity than a single diameter traverse, but it also has the effect of smoothing the data since it represents an averaging process.

Tables 8 and 9 show the data obtained on single diameter pitot tube traverses at low and high fuel feed rates. In Table 10 are summarized the experimental and theoretical velocities and volumetric flow rates for single traverses at both the high and low fuel feed rates.

The results of analyzing the single traverse data are shown in Table 11. For the experimental stack velocity, $V_{s_{avg}}$, since the earlier analysis indicated that Δp_{avg} and $(\sqrt{\Delta p})_{avg}$ are the dominant variables in determining precision of the estimate, only these two parameters were analyzed in the single traverse data.

TABLE 8. VELOCITY TRAVERSE DATA,
HOUSTON LIGHTING & POWER CO., T. H. WHARTON POWER PLANT,
UNIT NO. 1, LOW FUEL FEED RATE
Single Diameter Traverse

Date	Traverse Run No.	Time	Δp_{avg} (in H_2O)	$(\sqrt{\Delta p})_{avg}$ (in $H_2O)^{1/2}$	T_s °F	T_s °R	P_s in Hg	% H_2O	% CO_2	% O_2	M_d	M_s	V_s fps_{avg}	Q_s scf/hr x 10^{-6}
5/22/73	1-AE	1125-1135	0.22	0.475	265	725	29.84	13.9	8.1	6.6	29.5	27.9	29.1	4.59
"	2-AW	1145-1155	0.33	0.573	266	726	29.82	14.1	8.2	6.1	29.5	27.9	35.2	5.52
"	3-BE	1210-1220	0.25	0.494	254	714	29.82	14.4	8.4	5.1	29.5	27.8	30.1	4.80
"	4-BW	1225-1235	0.32	0.547	250	710	29.82	14.7	8.6	4.8	29.5	27.8	33.2	5.29
5/23/73	9-AE	1025-1030	0.23	0.475	252	712	29.78	13.3	7.7	7.0	29.5	28.0	28.8	4.65
"	10-AW	1035-1047	0.26	0.521	258	718	29.77	13.6	7.9	6.0	29.5	27.9	31.8	5.07
"	11-BE	1055-1108	0.27	0.515	251	711	29.77	14.2	8.3	5.9	29.5	27.9	31.4	5.03
"	12-BW	1115-1130	0.26	0.510	250	710	29.77	13.8	8.0	6.6	29.5	27.9	31.0	4.98
"	13-AW	1135-1145	0.27	0.522	263	723	29.77	14.5	8.6	6.8	29.6	27.9	32.1	5.03
"	14-AE	1151-1200	0.26	0.512	264	724	29.77	13.5	7.8	5.9	29.4	27.9	31.4	4.98

TABLE 9. VELOCITY TRAVERSE DATA,
HOUSTON LIGHTING & POWER CO., T. H. WHARTON POWER PLANT,
UNIT NO. 1, HIGH FUEL FEED RATE
Single Diameter Traverse

Date	Traverse No.	Time	Δp_{avg} (in H_2O)	$(\sqrt{\Delta p})_{avg}$ (in $H_2O)^{1/2}$	T_s °F	T_s °R	P_s in Hg	% H_2O	% CO_2	% O_2	M_d	M_s	$V_{s_{avg}}$ fps	Q_s scf/hr x 10^{-6}
5/22/73	5-BW	1400-1412	0.91	0.951	306	766	29.80	14.9	8.8	5.2	29.6	27.9	60.0	8.84
"	6-BE	1415-1425	0.85	0.873	308	768	29.80	14.9	8.8	5.7	29.6	27.9	55.1	8.09
"	7-AW	1428-1440	0.84	0.911	317	777	29.80	14.8	8.7	5.4	29.6	27.9	58.1	7.54
"	8-AE	1445-1455	0.80	0.845	316	776	29.80	13.8	8.1	6.2	29.5	27.9	53.6	7.90
"	15-AE	1340-1348	0.90	0.943	286	746	29.73	14.7	8.6	4.8	29.5	27.8	58.9	8.92
"	16-AW	1353-1400	0.88	0.930	314	774	29.73	14.7	8.6	5.0	29.5	27.8	59.4	8.66
"	17-BE	1405-1415	0.88	0.935	310	770	29.73	19.6	9.3	4.6	29.6	27.3	60.0	8.30
"	18-BW	1418-1425	0.89	0.938	310	770	29.73	14.5	8.5	6.1	29.6	27.9	59.5	8.75

TABLE 10. EXPERIMENTAL AND THEORETICAL GAS VELOCITY AND VOLUMETRIC FLOW RATE - HOUSTON LIGHTING AND POWER COMPANY, T. H. WHARTON PLANT, UNIT NO. 1
Single Diameter Traverse

Traverse No.[1]	Fuel Gas[2] Feed Rate MCFH	Load, megawatts	Stack Gas Velocity, fps		Volumetric Flow Rate, scf/hr x 10^{-6}	
			Experimental	Theoretical[3]	Experimental	Theoretical[4]
1-AE	390	41.5	29.1	33.3	4.59	5.26
2-AW	390	41.5	35.2	32.9	5.52	5.19
3-BE	390	41.5	30.1	31.7	4.80	5.07
4-BW	390	41.5	33.2	31.0	5.29	4.96
5-BW	680	71.0	60.0	57.1	8.84	8.44
6-BE	680	71.0	55.1	57.2	8.09	8.44
7-AW	680	71.0	58.1	58.5	7.54	8.54
8-AE	680	71.0	53.6	62.7	7.90	9.27
9-AE	385	39.0	28.8	33.7	4.65	5.46
10-AW	385	42.0	31.8	33.2	5.07	5.32
11-BE	385	40.0	31.4	31.5	5.03	5.07
12-BW	385	40.0	31.0	32.5	4.98	5.26
13-AW	385	40.0	32.1	31.4	5.03	4.95
14-AE	385	40.0	31.4	33.9	4.98	5.39
15-AE	680	71.0	58.9	56.7	8.92	8.64
16-AW	680	71.0	59.4	58.8	8.66	8.64
17-BE	680	71.0	60.0	55.3	8.30	7.99
18-BW	680	71.0	59.5	59.1	8.75	8.74

[1]Letters on run numbers are sample port designation per Figure 1.
[2]Fuel gas volume is in cubic feet at 60°F and 1 atmosphere pressure.
[3]Calculated by the procedure shown in Appendix 1, wet gas basis.
[4]Calculated by the procedure shown in Appendix 1, dry gas basis.

TABLE 11. STATISTICAL ANALYSIS, EXPERIMENTAL AND THEORETICAL STACK VELOCITIES AND RELATED PARAMETERS, SINGLE DIAMETER TRAVERSE

Fuel Feed Rate	Variable x	Mean $\bar{x}$	Variance s^2	Standard Deviation s	Percent Distribution About the Mean $\frac{2s \times 100}{\bar{x}}$ 95% Confidence Level
EXPERIMENTAL					
Low	V_s	31.4	3.58	1.89	12.2
	$\Delta_{p_{avg}}$	0.27	0.0012	0.035	25.8
	$(\sqrt{\Delta_p})_{avg}$	0.51	0.0009	0.030	11.6
High	V_s	58.1	5.82	2.4	8.3
	$\Delta_{p_{avg}}$	0.87	0.0013	0.036	8.2
	$(\sqrt{\Delta_p})_{avg}$	0.92	.0014	0.037	8.0
THEORETICAL					
Low	V	32.5	1.09	1.05	6.4
	$\%CO_2$	8.2	0.102	0.32	7.8
	T_s, ^oR	717	44.3	6.60	1.8
High	V	58.2	4.91	2.22	7.6
	$\%CO_2$	8.7	0.110	0.34	7.8
	T_s, ^oR	768	97.3	9.90	2.6

As can be seen by comparison of Tables 6 and 11, the results are considerably different when single diameter traverse data are analyzed and compared to the results obtained from analysis of Method 2 data. In Table 11, it can be seen that there is equality of variance for Δp_{avg}. When the data from two traverses are combined as specified in Method 2, equality of variance is not observed due to the smoothing of the data. For the Method 2 analysis, distribution about the mean for Δp_{avg} is $\pm$ 13.5 percent at the low level, while in the single traverse data the distribution about the mean for Δp_{avg} at the low level is $\pm$ 25.8 percent. However, at the high level, the corresponding distributions about the mean are $\pm$ 8.2 percent for single traverse data and $\pm$ 7.4 percent for the Method 2 data, indicating that the repeatability of the determination of Δp_{avg} is better at higher velocities, and little smoothing of data occurs by averaging data from two traverses.

Comparison of the analysis of $(\sqrt{\Delta p})_{avg}$ indicates that a similar apparent improvement in repeatability of $(\sqrt{\Delta p})_{avg}$ is obtained by averaging the results of two diameter traverses. For the Method 2 results, distribution about the mean for $(\sqrt{\Delta p})_{avg}$ is $\pm$ 3.9 and $\pm$ 4.3 percent at the low and high levels, respectively, while for the single traverse data, the similar values are $\pm$ 11.6 and $\pm$ 8.6, respectively. As can be seen, equality of variance is not obtained for $(\sqrt{\Delta p})_{avg}$, and the variance of $(\sqrt{\Delta p})_{avg}$ is a function of the level of $(\sqrt{\Delta p})_{avg}$.

Analysis of V_s for the single traverse data indicates that the distribution about the mean at the low and high levels is ± 12.2 and ± 8.3 percent, respectively, which corresponds closely with the distribution about the mean for $(\sqrt{\Delta_p})_{avg}$ at the low and high levels. This would be expected from the linear relationship between V_s and $(\sqrt{\Delta_p})_{avg}$ indicated by the correlation analysis described earlier.

Also shown in Table 11 are the results of analysis of the theoretical velocity, percent CO_2, and T_s based on single diameter traverse data. The relationships previously described indicating a major dependence in the distribution about the mean for V on the distribution about the mean for percent CO_2 still appear valid, with the apparent repeatability being somewhat poorer as shown by the increased distribution about the means for the single traverse data shown in Table 11, when compared to the similar data for Method 2 shown in Table 7.

3. Conclusions

Based upon this study, the following conclusions have been made. The experimental stack velocity and volumetric flow rate are primarily dependent upon the accuracy with which Δp is determined during the velocity traverse, over the velocity range studied. Under field conditions, using a Type S pitot tube and inclined manometer, measurements of Δp can be made which provide values of stack velocity with a percent distribution about the mean of $\pm$ 8.3 to $\pm$ 12.2, over the velocity range studied, based upon single diameter traverse data. The percent distribution about the mean for the velocity calculated according to Method 2 is $\pm$ 4.8 to $\pm$ 6.9 over the velocity range studied.

Even though velocities calculated according to Method 2 using data from two diameter traverses 90° apart have a smoothing effect on the data and shorten the distribution interval about the mean, when compared to single traverse data, accuracy analysis indicates that Method 2 as written provides reliable estimates of stack gas velocity at high flow rates, but that the estimates at low velocities are unreliable. This unreliability is directly attributable to the large variability in the determination of Δp at low velocities. Thus, if greater accuracy or repeatability in determining the experimental stack velocity is desired, the most profitable area for improvement would appear to be in improving the accuracy of measuring Δp in the stack.

METHOD 6 - SULFUR DIOXIDE

The sulfur dioxide section called for an investigation of possible variation in collection efficiency with changing concentration over the applicable range of the method and also for an investigation of the possibility of low recovery of sulfur dioxide due to retention in the isopropyl alcohol bubbler. Accordingly, a special experiment was designed to evaluate these effects along with some other relatively important factors. The details of the experiment and the results are given below.

Collaborative testing of this method is anticipated at the facilities of Walden Research and Monsanto Research, in accordance with plans and subcontract arrangements already submitted to the Project Officer. At the Dayton power plant, the only control of sulfur dioxide level which can be obtained is through the addition of dilution air to the flue gases. At Walden, control of the sulfur content of the fuel will make it possible to obtain varying SO_2 levels in the flue gas without dilution. For this reason, a collaborative test at each location is considered preferable.

Anticipated collaborators include Monsanto Research, Walden Research, Southwest Research Institute (Houston laboratory) and Southwest Research Institute (San Antonio laboratory). With some crowding, a fifth collaborator could be accommodated, and several air pollution control agencies are being contacted to see if a voluntary participant can be obtained.

To study the effect of the independent variables on the dependent variable (observed concentration expressed as a percent of the gas standard concentration), a quarter replicate factorial test plan was designed. Statistical analysis of the test data should identify which independent variables cause significant effects.

The independent variables studied were the sulfur dioxide concentration (397 ppm or 707 ppm), the number of sets of peroxide impingers in series (one or two), the number of isopropyl alcohol bubblers in series (one or two), the sampling time (20 or 30 minutes), and the sample volume (0.75 or 1.0 cubic feet). Variations in sample flow rate were thus accomplished. The dependent variable was defined as the observed concentration expressed as a percent of the expected value according to the gaseous standards which were used. Since the specific design used investigated seven variables in eight experiments, and only five were specified, the remaining two were dummy variables. The dummy variables are unassigned factors and are used to obtain an estimate of the variance. The combinations for each experiment are shown in Table 12 along with the value of the dependent variable.

Before discussing the results, it is important to clarify the independent variables and to describe the manner in which intermediate data were generated.

The two levels for the concentration were provided by two separate cylinders of sulfur dioxide in nitrogen (397 ppm and 707 ppm)

TABLE 12. FRACTIONAL-FACTORIAL EXPERIMENT DESIGN FOR FIVE VARIABLES IN EIGHT EXPERIMENTS SHOWING THE VALUES FOR EACH INDEPENDENT VARIABLE AND THE DEPENDENT VARIABLE

Experiment Number	IPA Bubblers	Peroxide Impingers	Concentration	Time	Volume	Observed Recovery
1	2	2 sets	707 ppm	20 min	0.75 ft^3	91.9%
2	1	2	397	30	1.00	99.7
3	1	1	397	20	0.75	100.3
4	1	2	707	20	1.00	94.5
5	1	1	707	30	0.75	94.5
6	2	1	707	30	1.00	90.7
7	2	1	397	20	1.00	97.0
8	2	2	397	30	0.75	102.8

which were analyzed (using the West-Gaeke method) by the supplier with accuracy of 0.5 percent quoted for each. The experiments were conducted shortly after receipt of the standard gases. Compatibility with system dynamics was achieved by charging a Tedlar bag from the respective cylinder and then sampling immediately from the bag. A commercially produced stack sampling apparatus was not available during the work; therefore, the train was assembled from individual components meeting the specifications shown in Figure 6-1 of Method 6 in the Federal Register. The probe and the pitot tube were not required for sampling from Tedlar bags.

For experiment numbers 3 and 5, the bubbler-impinger portion of the train was identical to Figure 6-1 of the method. In this configuration, measurements show the vacuum at the suction end of the train to be 17 to 20 inches of water for flow rates of 1 to 1.5 liters per minute. When two isopropyl alcohol bubblers were called for (experiment numbers 1, 6, 7, and 8), an additional bubbler containing 15 ml of 80 percent isopropyl alcohol was inserted in series into the train following the first isopropyl alcohol bubbler. When two sets of peroxide-filled midget impingers were called for (experiment numbers 1, 2, 4, and 8), two impingers charged with 15 ml of three percent hydrogen peroxide followed by one empty impinger were inserted in series into the train following the empty midget impinger. For example, experiment numbers 1 and 8 contained two midget bubblers charged with isopropyl alcohol

followed by two midget impingers charged with hydrogen peroxide followed by one empty midget impinger followed by two more peroxide impingers followed by another empty impinger.

The midget impingers charged with peroxide were treated in sets containing two filled impingers and one empty so that the procedure as described in Sections 4.2 and 4.3 of the method could be applied to each set independently. A result was thus generated and recorded for each set and the two were added and converted to the percentage of the expected value to produce the final result (the dependent variable). There is a distinct advantage in this approach since another independent estimation of collection efficiency can be made using experiment numbers 1, 2, 4, and 8 by comparing the contents of the second set of impingers with the first. These data are shown in Table 13, and the results will be discussed subsequently.

The contents of the isopropyl alcohol bubblers were not discarded as per the method but were analyzed for sulfur dioxide by an improvised procedure to oxidize any retained SO_2 to SO_3 and then determined by titration as in Section 4.3 of the method. The contents of each of the bubblers were analyzed separately, and results were expressed in terms of percent recovery of the gaseous sample so that a material balance of the entire train was easily accomplished by simple addition. These percentages were not added into the dependent

TABLE 13. INTERMEDIATE EXPERIMENTAL DATA FROM FRACTIONAL-FACTORIAL EXPERIMENT DESIGN

Experiment Number	IPA Bubblers* 1st	2nd	Peroxide Impingers* 1st	2nd	Total
1	1.1	1.7	91.7	0.2	91.9
2	0.5	-	99.0	0.7	99.7
3	0	-	100.3	-	100.3
4	0	-	94.5	0	94.5
5	2.0	-	94.5	-	94.5
6	1.0	0.1	90.7	-	90.7
7	0.5	0.5	97.0	-	97.0
8	0.8	2.5	102.8	0	102.8

*Numbers represent percentage of expected value based on concentration of gas standard.

variable. The data are shown in Table 13. In order to confirm that the contents of the bubblers represented retained SO_2 rather than any SO_3 present in the sample, a series of experiments was run in which the bubbler contents were not oxidized but rather titrated directly so that any sulfur oxides detected would be attributable to SO_3 rather than retained SO_2. The results (not shown) showed no detectable SO_3 in any of the bubblers in any of eight runs. Therefore, the respective results shown in Table 13 are assured to be due to SO_2 retention. These results will be discussed in more detail later.

The two levels of time and sample volume are straightforward. The actual selection of the times and volumes are based on the minimum time and minimum volume as designated in the Federal Register under Section 60.46(c)(2), Test Methods and Procedures. The various combinations of sample time and sample volume produce flow rates of 0.71, 0.94, 1.06, and 1.42 liters per minute.

Mechanical difficulties were encountered throughout the experiments, necessitating the repeating of some of the runs one or more times. These difficulties were associated with pump leakage, meter malfunction, or loose connections. It is, therefore, very important to make the leak check as described in Section 4.1.1 of the method.

Another difficulty encountered was in the carryover of isopropyl alcohol which often occurred at sample flow rates which were about 1.4 liters per minute (1 cu ft in 20 min) such as in experiment numbers 4 and 7.

The results of the statistical analysis are given in Table 14. The table shows the net effect [the difference between the average value of responses at the high (+) level and the average value of responses at the low (-) level] for each variable. The significance of each effect (with respect to the dependent variable) is indicated by the absolute value of the t-statistic and the corresponding percentage probability. The significance percent for each effect thus provides an estimate of the probability of finding an effect that large due to chance or experimental

TABLE 14. STATISTICAL ANALYSIS OF FRACTIONAL-FACTORIAL DESIGN

Youden Ruggedness Test*

Plackett-Burman Design for 7 Factors and 8 Experiments*

System - Method 6

Response - Recovery

Variable No.	Variable Name	Effect (- to +)	|t| - Value	Significance Percent
1	Dummy	-1.30	0.85	42
2	IPA Bubblers	-1.65	1.08	32
3	Impingers	-1.60	1.05	34
4	Dummy	1.55	1.02	35
5	Concentration	-7.05	4.62	0.8
6	Time	1.00	0.65	>50
7	Volume	-1.90	1.24	25

Average value of response = 96.425

Standard error = 1.5266

Degrees of freedom = 2

*Youden, W. J., "The Collaborative Test," J. of the A.O.A.C., 46, No. 1, (1963), pp 55-62.

Plackett, R. L. and Burman, J. P., "Design of Optimum Multifactoral Experiments," Biometrika, 33, (1946), pp 305-325.

error alone. If the effects of one or more dummy variables were significant, there would be either (1) significantly large interactions of main effects, (2) important independent variables omitted or not held constant, or (3) considerable error in the measurement technique.

The only effect sufficiently large to be significant (10 percent level of significance) is the concentration. The effect is negative, indicating a decreased response in going from the low level to the high level. In the absence of data from the second set of peroxide impingers from experiment numbers 1 and 4, this might be interpreted as a decrease in collection efficiency at the higher concentration level. Since the second set of impingers contains little or no sulfur dioxide (see also experiment numbers 2 and 8 at the lower concentration level), plus the fact that there is not a sufficiently significant effect from peroxide impingers (the effect is even in the wrong direction), the natural conclusion is that the higher concentration is very probably in the neighborhood of 660 ppm. The importance of retrieval of intermediate data now becomes evident.

To summarize the results thus far: there are no significant effects due to isopropyl alcohol bubblers, peroxide impingers, time, volume, or dummy variables. The effects of concentration are either a concentration bias in the method or an inaccuracy in the concentration of the 707 ppm cylinder. Unfortunately, at the time of report preparation, the 707 ppm standard was no longer available for independent analysis.

The effects of sulfur dioxide retention in the isopropyl alcohol bubblers are negligible from the analysis above and are also minor according to the data in Table 13. The average retention in a bubbler is less than one percent of the amount present (average of 0.9 percent for 12 observations). The values can be seen to range from zero to 2.5 percent at the highest. All of these results were obtained using the 15-minute purge as specified in Section 4.1.2 of the method. A single experiment (under the same conditions as experiment number 1) in which the purge was not done showed 7 percent retention in each of the two bubblers for a total of 14 percent. It is, therefore, quite important to follow the purging procedure rigorously.

The minimum detectable limit (based on a net titration of 0.1 ml, a 0.75 ft^3 sample, and a 10 ml aliquot) is 3 ppm which should cause no limitations in the use of the method. If more sensitivity was desired, a larger sample could be taken. The method can conveniently analyze samples up to 1400 ppm (based on 50 ml titration, 0.75 ft^3 sample, 10 ml aliquot), providing the collection efficiency does not deteriorate at that level.

METHOD 7 - NITROGEN OXIDES

Laboratory work was conducted to check out the entire procedure and especially to investigate the reported interference from hydrogen chloride. A total of 64 experimental tests were made using standard nitric oxide mixtures of 98 and 700 ppm.

In 48 tests comprising five sets of experiments, the 98 ppm standard gas was used as a test gas in flasks which were spiked with hydrogen chloride of known concentration. Concentrations of hydrogen chloride were 11 ppm, 50 ppm, 100 ppm, 500 ppm, and 1120 ppm. In two sets, the spiking was done using hydrochloric acid of known concentration while in the other three sets, spiking was accomplished by injecting the proper amount of dry hydrogen chloride gas.

In 16 other tests, the 700 ppm test gas was used, half without hydrogen chloride and half with the addition of sufficient hydrochloric acid to give a hydrogen chloride concentration of 700 ppm. All samples were analyzed according to the procedures described in EPA Method 7.

Table 15 and Figure 2 presents the results obtained. Based on these results and the complete laboratory data, the following conclusions are established concerning Method No. 7:

1. The method is tedious and time consuming, especially in the analytical phase. This, of course, was known previously and has been the subject of some discussion and comment.

TABLE 15. DATA TABULATION--INTERFERENCE OF HYDROGEN CHLORIDE WITH NO_x DETERMINATION - EPA METHOD NO. 7

Date	Set	Chloride Source	HCl Conc. by Vol. ppm	Sample Serial No.	ANALYSIS: Stand. NO ppm Vol.	ANALYSIS: Spiked NO Conc. ppm	ANALYSIS: Unspiked NO Conc. ppm
11/16/72	1	hydrochloric acid	1120	1	98	--	110
				2	98	--	121
				3	98	--	--
				4	98	--	116
				5	98	15	--
				6	98	20	--
				7	98	20	--
				8	98	--	--
				Avg.	98	18	
11/20/72	2	hydrochloric acid	11	9	98	--	103
				10	98	--	112
				11	98	--	108
				12	98	--	105
				13	98	95	--
				14	98	97	--
				15	98	94	--
				16	98	97	--
				Avg.	98	96	
11/21/72	3	dry hydrogen chloride	500	17	98	61	--
				18	98	65	--
				19	98	52	--
				20	98	56	--
				21	98	73	--
				22	98	83	--
				23	98	--	--
				24	98	61	--
11/27/72			500	25	98	--	102
				26	98	--	100
				27	98	--	97
				28	98	--	95
				29	98	69	--
				30	98	62	--
				31	98	55	--
				32	98	62	--
				Avg.	98	64	

Table 15. Data Tabulation--Interference of Hydrogen Chloride with NO_x Determination - EPA Method No. 7 (Cont'd.)

Date	Set	Chloride Source	HCl Conc. by Vol. ppm	Sample Serial No.	ANALYSIS Stand. NO ppm Vol.	ANALYSIS Spiked NO Conc. ppm	ANALYSIS Unspiked NO Conc. ppm
11/29/72	4	dry hydrogen chloride	100	33	98	--	89
				34	98	--	91
				35	98	--	91
				36	98	--	90
				37	98	83	--
				38	98	82	--
				39	98	79	--
				40	98	82	--
				Avg.	98	82	
12/5/72	5	dry hydrogen chloride	50	41	98	--	91
				42	98	--	92
				43	98	--	92
				44	98	--	90
				45	98	91	--
				46	98	88	--
				47	98	89	--
				48	98	89	--
				Avg.	98	89	
12/6/72	6	hydrogen chloride	700	49	700	--	943
				50	700	--	841
				51	700	--	917
				52	700	--	847
				53	700	447	--
				54	700	412	--
				55	700	502	--
				56	700	469	--
12/11/72		hydrogen chloride	700	57	700	--	602
				58	700	--	--
				59	700	--	712
				60	700	--	545
				61	700	--	--
				62	700	429	--
				63	700	521	--
				64	700	409	--
				Avg.	700	456	

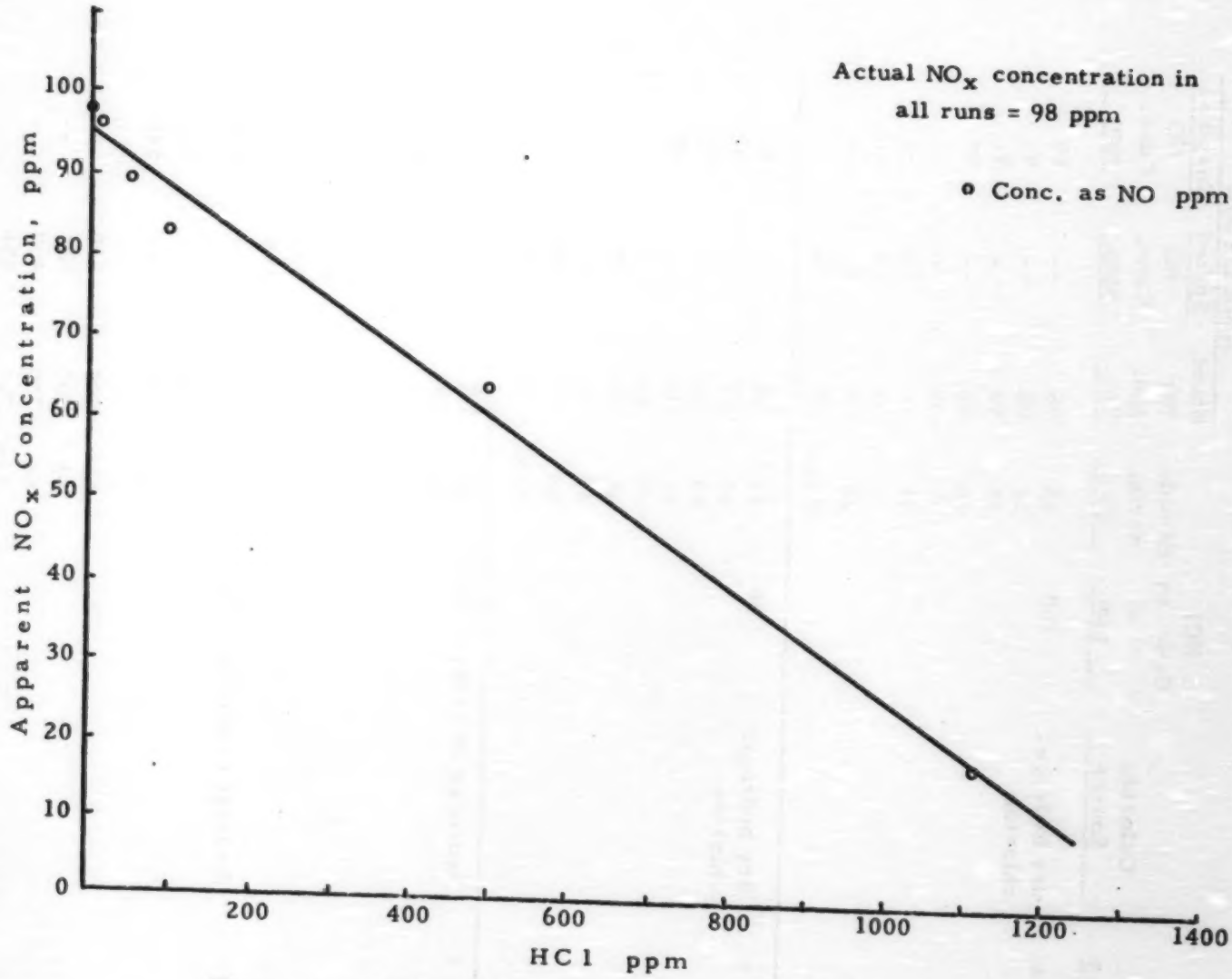

Figure 2. Interference of HCl With the Determination of NO_x – EPA Method No. 7, Average Points

2. Results are affected by the presence of hydrogen chloride, as has been indicated by previous publications. The degree of interference is approximately linear with hydrogen chloride concentration, ranging as high as 78 percent with 1120 ppm HCl when sampling a test gas of approximately 100 ppm NO_x. A similar relationship appears to apply in the case of the 700 ppm test gas, although tests were only run at a single level of HCl, 700 ppm. At this level, the indicated NO_x level is about 65 percent of the original value as determined in tests without hydrogen chloride. It should be noted that erratic results were obtained with the unspiked 700 ppm samples.

The sensitivity of the method along with the minimum detectable limits for NO_x by this method have been estimated. Data used in the calculations of the minimum detectable limit were taken from a calibration curve constructed by analysis of a series of standard solutions of potassium nitrate. Concentration range of the standards was zero to 400 μg nitrogen dioxide. Measured absorbance of the solutions was in the range of 0-0.5 absorbance units, using absorbance cells of 1.2 centimeter path length. The calculations are presented in Appendix III. The minimum detectable limit is estimated to be 2 ppm NO_x as NO_2 in the gas sample. The upper limit without dilution is about 100 ppm NO_x as NO_2 in the gas sample. To analyze gas samples containing around 700 ppm NO_x would require a tenfold dilution according to Section 4.3.1 of the method (Appendix III, Figure 1).

The maximum sensitivity of the method can approach 0.2 ppm NO_x provided the absorbance can be read to 0.001 absorbance units, but in a practical sense would probably be between 0.2 and 2.0 ppm NO_x.

APPENDIX I

Glossary of Terms and Equations

A. Terms and equations taken from The Federal Register, Volume 36, December 23, 1971:

Equations

$(V_s)_{avg}$ = Average Stack Gas Velocity, ft/sec

$$(V_s)_{avg} = K_p C_p \left(\sqrt{\Delta_p}\right)_{avg} \sqrt{\frac{(T_s)_{avg}}{P_s M_s}}$$

Q_s = Stack Gas Volumetric Flow Rate, ft^3/hr

$$Q_s = 3600\,(1 - B_{wo}) \left(\frac{T_{std}}{(T_s)_{avg}}\right)\left(\frac{P_s}{P_{std}}\right) V_s A$$

Terms

K_p = Conversion constant : $K_p = 85.48 \frac{ft}{sec} \left(\frac{Lb}{Lb\text{-}mole\ ^oR}\right)^{1/2}$

C_p = Pitot tube coefficient, dimensionless

$\Delta_{p_{avg}}$ = Average velocity head of stack gas

$$\Delta_{p_{avg}} = \frac{1}{n} \sum_{i=1}^{i=n} \Delta_{p_i}, \text{ where } n = \text{number of traverse points}$$

$\left(\sqrt{\Delta_p}\right)_{avg}$ = Average of the square roots of the velocity head measurements taken at individual traverse points

$$\left(\sqrt{\Delta_p}\right)_{avg} = \frac{1}{n} \sum_{i=1}^{i=n} \sqrt{\Delta_{p_i}}, \text{ where } n = \text{number of traverse points}$$

$(T_s)_{avg}$ = Average absolute stack gas temperature, ^{o}R

$$(T_s)_{avg} = \frac{1}{n} \sum_{i=1}^{i=n} T_i, \text{ where } n = \text{number of traverse points}$$

T_{std} = Absolute temperature at standard conditions, $530^{o}R$

P_s = Absolute stack gas pressure, inches mercury

P_{std} = Absolute pressure at standard conditions, 29.92 inches mercury

B_{wo} = Proportion by volume of water vapor in the stack gas

M_d = Dry molecular weight of the stack gas (calculated from Orsat analytical data)

M_s = Molecular weight of the stack gas, wet basis

$$M_s = M_d (1 - B_{wo}) + 18 B_{wo}$$

B. Terms and equations used in statistical analysis of data:

$$\text{Correlation Coefficient} = \frac{\sum_{i=1}^{n} (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{n} (x_i - \bar{x})^2 \sum_{i=1}^{n} (y_i - \bar{y})^2}}$$

where x is the independent variable and y is the dependent variable, i.e. $y = f(x)$

$\bar{x}$ is the arithmetic mean of variable x

$$\bar{x} = \frac{1}{n} \sum_{i=1}^{i=n} x_i, \text{ where } n \text{ is the sample size}$$

s^2 is the unbiased estimate of the population variance, σ^2

$$s^2 = \frac{1}{n-1} \sum_{i=1}^{n} (x_i - \bar{x})^2, \text{ where } \bar{x} \text{ and } n \text{ as above}$$

is the sample standard deviation

$$s = \sqrt{s^2}$$

Percent distribution about the mean, 95 percent confidence level is defined as

$$\frac{2s \cdot 100}{\bar{x}}, \text{ s and } \bar{x} \text{ as above}$$

t-value is a student's t with six degrees of freedom

$$t = \frac{\text{effect}}{\text{standard error}}$$

C. Conversion Factors:

inches x 2.540 = centimeters

cubic feet/unit time x 0.0283 = cubic meters/unit time

feet per second x 0.3048 = meters per second

pounds/unit time x 0.4536 = kilograms/unit time

feet x 0.3048 = meters

APPENDIX II

DATA FROM T. H. WHARTON POWER PLANT, HOUSTON LIGHTING AND POWER COMPANY

Sample calculation of theoretical stack velocity and volumetric flow rate.

Carbon in fuel gas, calculated from gas chromatographic analysis: 1.072 lb-atom carbon/lb-mole fuel gas.* Carbon in stack gas, from Orsat Analysis Run 1-AE, Table 1: 0.081 lb-atom carbon/lb-mole stack gas.

mole dry stack gas/mole fuel gas in:

$$\frac{1.072}{0.081} = 13.24$$

moles H_2O = 2 x moles CO_2 = 2 x 0.081 = 0.162

Total moles stack gas/mole fuel gas in:

$$13.24 + (0.162)(13.24) = 1.162 \times 13.24 = 15.38$$

Theoretical gas velocity, wet basis:

$$\frac{\text{Total moles stack gas}}{\text{moles fuel gas in}} \times \frac{\text{Fuel feed rate, ft}^3\text{/hr}}{(\text{Stack area, ft}^2)(3600 \text{ sec/hr})} \times \frac{T_s}{T_{\text{fuel gas}}}$$

$$= 15.38 \frac{\text{moles stack gas}}{\text{moles fuel gas in}} \times \frac{390 \times 10^3 \text{ ft}^3\text{/hr}}{(69.81 \text{ ft}^2)(3600 \text{ sec/hr})} \times \frac{725^\circ R}{520^\circ R}$$

$$= 33.3 \text{ fps}$$

Theoretical volumetric flow rate, dry basis:

$$\frac{\text{moles dry stack gas}}{\text{moles fuel in}} \times \text{fuel feed rate, ft}^3\text{/hr} \times \frac{530^\circ R}{T_{\text{fuel gas}}}$$

where:

$530^\circ R = 70^\circ F$ = EPA specified temperature

$$13.24 \frac{\text{moles dry stack gas}}{\text{moles fuel in}} \times 390 \times 10^3 \text{ ft}^3\text{/hr} \times \frac{530^\circ R}{520^\circ R}$$

$$= 5.26 \times 10^6 \text{ ft}^3\text{/hr.}$$

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* 96.2% methane.

APPENDIX III

Estimation of Limits for NO_x by Method 7

The approximate minimum detectable limit for NO_x by Method 7 can be estimated from laboratory data and the appropriate equations for calculating the concentration of nitrate in the samples.

Ref.: Method 7, Section 6.2, Federal Register, Vol. 36, p. 24893, 23 December 1971.

$$C = \frac{m}{V_{sc}} \left(\frac{\frac{1 \text{ lb}}{\text{cu ft}}}{1.6 \times 10^4 \mu g/ml} \right) = \left(6.2 \times 10^{-5} \frac{\text{lb/scf}}{\mu g/ml} \right) \left(\frac{m}{V_{sc}} \right)$$

where C = conc. of NO_x (as NO_2), lb/scf

m = mass of NO_2 in gas sample, μg

V_{sc} = sample volume at standard conditions, ml.

V_{sc} = 200 ml

According to Sections 3.3.4 and 5.2, the calibration curve is prepared using diluted standard solutions with a concentration range of $0 \leq m \leq 400$ μg. The resulting calibration curve in our laboratory gives 806 μg NO_2/absorbance unit, using absorption cells of 1.2 cm path length. Therefore, an absorbance of 0.010 is equivalent to 8.06 μg NO_2 and

$$C = \frac{6.2 \times 10^{-5} (8.06)}{2000} = 25 \times 10^{-8} = 0.25 \times 10^{-6}$$

$$\text{ppm} = C \frac{\text{lb}}{\text{ft}^3} \times \frac{359 \text{ ft}^3/\text{lb-mole}}{46 \text{ lb/lb-mole}} \times \frac{530^\circ R}{492^\circ R} \times \frac{10^6 \text{ ft}^3}{\text{million ft}^3}$$

$$\text{ppm} = C \times (8.4 \times 10^6)$$

$$\text{ppm} = (0.25 \times 10^{-6}) \times (8.4 \times 10^6) = 2.1 \text{ ppm}$$

A concentration of 2 ppm NO_2 in the gas sample is probably detectable.

A maximum sensitivity of about 0.2 ppm is possible if absorbance can be measured to 0.001 absorbance unit.

As shown in Figure 1, the upper limit of gas sample NO_x concentration without dilution is about 100 ppm based on an absorbance of 0.5 unit.

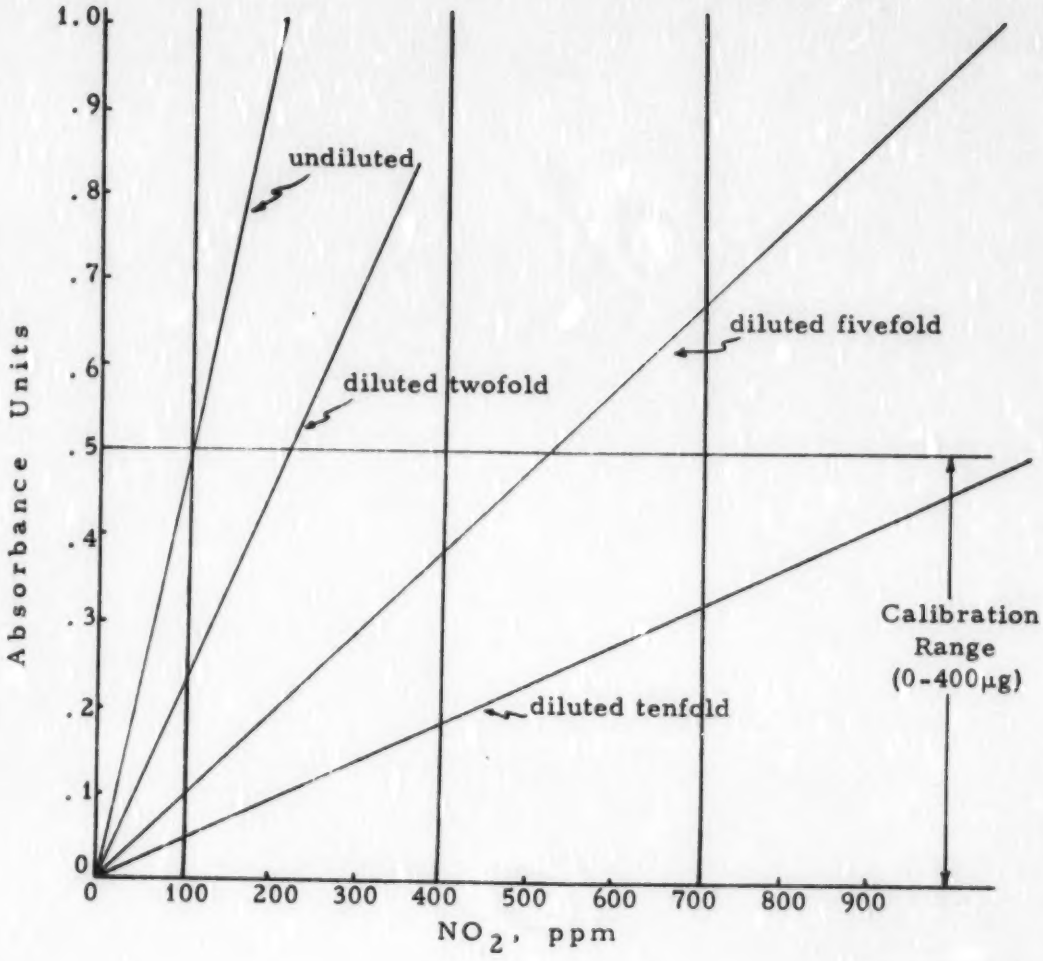

FIGURE 1. STANDARD AND DILUTED CALIBRATION CURVES FOR NO_x DETERMINATION

APPENDIX IV

Accuracy of Method 2

To assess the acuracy of the experimentally determined Method 2 stack gas velocities with respect to the theoretical stack gas velocities, a Student's t-test is used to obtain a significance level.

Assume $\bar{V}_{theoretical}$ represents the true stack gas velocity. Then, using a calculated t-value

$$t_c = \frac{\bar{V}_{s_{avg}} - \bar{V}_{theoretical}}{s/\sqrt{n}}$$

where s is the sample standard deviation of $V_{s_{avg}}$ and n is the number of observations of $V_{s_{avg}}$ used to obtain $\bar{V}_{s_{avg}}$.

The significance level resulting from the test will be the probability of obtaining a sample (experimental) mean $\bar{V}_{s_{avg}}$ which differs from the true (theoretical) mean $\bar{V}_{theoretical}$ by a magnitude of $|\bar{V}_{s_{avg}} - \bar{V}_{theoretical}|$ or greater due to chance alone. The probability is obtained from a table of Student's t distribution with $(n - 1)$ degrees of freedom. A low significance level, less than 10 percent, indicates that $\bar{V}_{s_{avg}}$ is not a good estimate of $\bar{V}_{theoretical}$.

1. Low Level

The hypothesis to be tested is that $\mu = 32.5$ ($\bar{V}_{theoretical}$). From Table 6 , $\bar{V}_{s_{avg}} = 31.4$ with a sample standard deviation $s = 0.756$.

Then,

$$t_c = \frac{31.4 - 32.5}{(0.756)/\sqrt{5}}$$

$$t_c = \frac{-1.1}{0.337}$$

$$t_c = -3.264 \text{ with 4 degrees of freedom}$$

From the Student's t table, the percent significance level for $t_c = -3.264$ with four degrees of freedom is 3.49%.

2. High Level

The hypothesis to be tested is that $\mu = 57.4$ ($\bar{V}_{theoretical}$). From Table 6, $\bar{V}_{s_{avg}} = 58.1$ with a sample standard deviation $s = 2.015$. Then,

$$t_c = \frac{58.1 - 57.4}{(2.015)/\sqrt{4}}$$

$$t_c = \frac{0.7}{1.0075}$$

$$t_c = 0.695 \text{ with 3 degrees of freedom}$$

From the Student's t table, the percent significance level for $t_c = 0.695$ with three degrees of freedom is 56.08%.